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(54) **REFLECTION FILM AND TRANSLUCENT REFLECTION FILM FOR OPTICAL INFORMATION RECORDING MEDIUM, OPTICAL INFORMATION RECORDING MEDIUM, AND SPUTTERING TARGET FOR OPTICAL INFORMATION RECORDING MEDIUM**

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a Ag based alloy reflection film or translucent reflection film for an optical information recording medium capable of imparting high reliability to obtain a high multiple speed DVD and a next-generation optical disk by finding an Ag based alloy having high thermal conductivity, high reflectance and high durability compared with pure Ag and a conventional Ag alloy.
SOLUTION: The Ag based alloy containing 0.005 to 0.40% (at%) Bi and/or Sb in total is used. The reflection film and the translucent reflection film of the Ag based alloy having such a composition has high reflectance, high thermal conductivity and high durability.

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Assignee: Kobe Steel Co., Japan
Inventor: Yuuki Tauchi et al.

Title of Invention: **Reflective film for photo information memory medium and semi-transparent reflective film, photo information memory medium and sputtering target for photo information memory medium**

[Abstract]

[Problems] New type of Ag-based alloys were developed having better properties including high thermal conductivity, high reflectivity and high endurance when compared to pure Ag or conventional Ag-based alloys. Utilizing such newly developed alloys, the present invention provides Ag-based reflective film or semi-transparent reflective film for photo information memory medium with high reliability which can be further value-added to high-speed DVD or next generation photo discs. Moreover the invention provides Ag-based sputtering target which is used for film fabrication of aforementioned reflective film and semi-transparent reflective film, and photo information medium having such reflective film or semi-transparent reflective film.

[Methods] The aforementioned films and media can be achieved by using Ag-based system being alloyed with Bi and/or Sb element(s) within a range from 0.005atomic % to 0.40atomic % in total of Bi and/or Sb element(s).

[What is Claimed]

1. A Ag-based alloy reflective film or semi-transparent reflective film for photo information memory medium; which the alloy has alloying element(s) of Bi and/or Sb

with total of 0.005 ~ 0.40 atomic %.

2. The Ag-based alloy reflective film or semi-transparent reflective film for photo information memory medium cited in claim 1, wherein the aforementioned Ag-based alloy contains at least one element from a element group of rare earth elements.
3. The Ag-based alloy reflective film or semi-transparent reflective film for photo information memory medium cited in claim 2, wherein the said rare earth element is Nd and/or Y.
4. The Ag-based alloy reflective film or semi-transparent reflective film for photo information memory medium cited in claim 3, wherein the total amount of aforementioned rare earth elements of Nd and/or Y should be 0.1 ~ 2 atomic %.
5. The Ag-based alloy reflective film or semi-transparent film for photo information memory medium cited in any one of claims 1, 2, 3 or 4, wherein the said Ag-based system is alloyed with at least one type of elements from an alloying element group comprising of Cu, Au, Rh, Pd and Pt with total amount of 0.1 ~ 3 atomic %.
6. A Ag-based alloy sputtering target for photo information memory medium; which the alloy has Bi as an alloying element with 0.05 ~ 4.5 atomic %.
7. A Ag-based alloy sputtering target for photo information memory medium, which the alloy has Sb as an alloying element with 0.005 ~ 0.40 atomic %.
8. A photo information memory medium which is furnished with the Ag-based alloy reflective film cited in any claim 1 through 5.
9. A photo information memory medium which us furnished with the Ag-based semi-transparent reflective film cited in any claim1 through 5.

[Detailed Drawings of The Invention]

[Technology in which This Invention is Involved]

This invention, in a technical field of photo information memory media such as CD (compact disc) or DVD (digital versatile disc), is directly related to reflective film and semi-transparent reflective film, used for photo information memory medium, having a high thermal conductivity, high reflectivity and high endurance. The invention also provides sputtering target for photo information memory medium which is used for film

fabrication of reflective film as well semi-transparent reflective film, and photo information memory medium which is furnished with aforementioned reflective film and semi-transparent reflective film.

[Prior Art Technology]

There are several types in the photo information memory media (or photo disc); they can include (1) read-out only type, (2) write-add type, and (3) editable (read and write) type.

Firstly, the read-out only type disc has a laminated structure of reflective (metallic) film main being consisted of Al, Ag, Au, or the like being deposited onto the transparent plastic (for example, polycarbonate etc.) base substrate which is uneven pits (for memory data) are formed. The memorized data can be read-out (or reproduced) by detecting reflectivity differences or phase differences of the laser light which is irradiated to the disc. For such a photo disc, there are two types; (1) one-side mono-layer type, which is comprised of transparent plastic base substrate to which the reflective film was fabricated, and (2) one-side double-layer type, for increasing memory capacity, which is constructed with a transparent plastic base substrate to which the reflective film is formed and the plastic substrate is bonded with the semi-transparent film with an appropriate adhesive agent. CD-ROM and DVD-ROM are examples of photo discs which are fabricated through the 2nd type of disc.

Secondly, the write-add type disc is a laminated structure of transparent plastic base substrate on which the memory film (organic pigment film) and reflective film (metallic film) are formed. With this type of photo disc, the irradiated light heats and decomposes the memory film to deform the grove (which is a guide-groove provided on the base substrate in advance), resulting in that data can be memory-stored. At the same time, the differences in reflectivity between the decomposed portion and un-decomposed portion of the base substrate are detected by the laser light, so that the memory-stored data can be retrieved and reproduced. It is a characteristics with this type of photo disc that memory-stored data can not be overwritten (in other words, one time recording and many times reproduction), and CD-R, DVD-R, DVD+R are typical examples using this type of photo disc.

The read-write (editable) type photo disc has a basic laminated structure of a transparent plastic film on which the conductive protective film/memory film/conductive protective film/reflective (metallic) film are formed. Using the reversible phase transformation between crystalline phase and non-crystalline (amorphous) phase of the memory film by the laser light irradiation, data can be memory-stored. Memory-stored data can be reproduced (retrieved) by detecting by the laser light differences in reflectivity between the crystalline and non-crystalline phases of the memory film. It is a characteristics of this type of photo disc that data can be rewritten from thousand to hundred thousand times. CD-RW, DVD-RAM, DVD-RW, and DVD+RW are typical examples of this type of photo disc.

For the aforementioned three types of photo discs, alloys having Au, Al, Ag or the like elements as main constituents are principally used for reflective film and semi-transparent reflective film, owing their physical properties including thermal conductivity, reflectivity as well as endurance.

Since, among of these, Au-system reflective film (in which Au element is a main chemical composition) possesses excellent endurance (for both chemical and thermal stabilities), the memory-reproduction property of the photo disc is hardly age-deteriorated. However, the Au-system reflective film has technical drawbacks; (1) the raw material price is high, and (2) desired high reflectivity by the blue-violet laser (wavelength: 405 nm) for the next generation disc (for example, blue- ray disc, etc.) can not be achieved.

On the other hand, the raw material's cost for Al used in the Al-system reflective film is relatively low, so that the remarkable cost-down can be achieved as the photo disc price. Moreover, the Al-system reflective film exhibits the high reflectivity against the blue-violet laser. However, when compared to Au-system reflective film, Al-system reflective film has relatively lower endurance characteristics, and high thermal conductivity (which is required as a film property when used for write-add and overwrite photo type discs) can not be obtained.

Ag-system reflective film containing Ag element as its major chemical constituent possesses high reflectivity against the blue-violet laser ray which is required for the next generation photo disc, high thermal conductivity which is also required for the write-add and overwrite editable type discs, and is less expensive than Au-system reflective film.

Hence expectations on Ag-system reflective film as reflective film or semi-transparent reflective film are growing. However, although its endurance is better than the Al-system reflective film, Ag-system does not receive an equivalent evaluation to Au-system reflective film. Accordingly, in order to develop and realize the Ag-system reflective film as promising reflective film as well as semi-transparent reflective film, improvements on endurance are inevitable without loosing its original excellent high reflectivity as well as high thermal conductivity.

For such improvements, the followings are reported. For example, Patent Article 1 discloses addition of Au, Pd, Cu, Rh, Os, Ir, and Pt to Ag parent phase, and Patent Article 2 discloses addition Pd and Cu to Ag to enhance the endurance (chemical stability). Moreover, present inventors have proposed to add rare earth elements to Ag to enhance the endurance (thermal stability by controlling the grain growth), as disclosed in Patent Article 3. However, the high-speed memory DVD or the next generation photo disc demands further higher reflectivity, so that further developments and improvements on high endurance and high thermal conductivity as well as high reflectivity are urgently required.

With regard to the endurance property, the high corrosion resistance against the halogen elements including chlorine ion is highly required. This requirement is very specific for the write-add type photo disc in which organic pigment memory film containing halogen element, protective film, adhesive agent layer and reflective film are directly laminated to each other. Furthermore, unlike the DVD, the next generation photo disc has a reverse-laminated structure in which the reflective film is firstly formed on the transparent plastic base substrate, then conductive film/memory film/conductive film are laminated. Therefore, it is required that (1) the surface roughness should be extremely small to control the deterioration of memory-reproduction properties and (2) the stability of surface roughness should be maintained even if the surface was subjected to thermal loading.

For thermal conductivity, it is necessary for the heat which was generated within the extremely small area of the memory film by the laser light irradiation to dissipate and diffuse as fast as possible, the high thermal conductivity is also required for the reflective film to function as a heat diffusing film, too.

Moreover regarding to the reflectivity, the reflective film should possess the high reflectivity against the blue-violet laser to meet needs arisen from the high-speed DVD or the next generation photo discs.

However, there are no Ag-based alloys available so far which can meet all aforementioned requirements. Hence, it is highly required to develop new Ag-based alloys which possess and meet all requirements including high thermal conductivity, high reflectivity, better endurance to maintain the high reliability for the high-speed DVD or the next generation photo discs.

[Patent Article 1]

US Patent 60,007,889 specification, and claims

[Patent Article 2]

Tokkai Hei 6-208732, claims, and

"On the other hand, the raw material's cost for Al used in the Al-system reflective film is relatively low, so that the remarkable cost-down can be achieved as the photo disc price. Moreover, the Al-system reflective film exhibits the high reflectivity against the blue-violet laser. However, when compared to Au-system reflective film, Al-system reflective film has relatively lower endurance characteristics, and high thermal conductivity (which is required as a film property when used for write-add and overwrite photo type discs) can not be obtained.", as previously mentioned.

[Patent Article 3]

Tokkai 2002-15464, and claims

[Items which This Invention Intended to Solve]

Based on the aforementioned technical problems associated with the conventional types of thin films, the objectives of this invention were to develop and discover the Ag-based alloys with higher thermal conductivity, higher reflectivity and higher endurance than pure Ag and conventional Ag-based alloys, and to provide Ag-based alloy reflective film or semi-transparent reflective film used for the photo information memory medium

having high reliability for the high-speed DVD or the next generation photo discs, Ag-based alloy sputtering target used for a photo information memory medium used for forming the said Ag-based alloy reflective film or semi-transparent reflective film, and a photo information memory medium being provided with the said reflective film or semi-transparent reflective film.

[Methods for Solving Problems]

The reflective film or semi-transparent reflective film used for the photo information memory medium (or photo disc) according to this invention is composed of Ag-based alloy containing 0.005 ~ 0.40 atomic % as total of Bi and/or Sb element(s). Such newly developed Ag-based alloy exhibits high reflectivity, high thermal conductivity, and high endurance.

More preferably, the said Ag-based alloy should contain al least one element selected from an element group comprising of rare earth elements. The Ag-based alloy containing Nd and/or Y shows excellent endurance property (particularly, thermal stability). It is preferable to control the total amount of Nd and/or Y within in 0.1 ~ 2 atomic %.

It was found that it was also effective to add at least one element chosen from the element group comprising of Cu, Au, Rh, Pd, and Pt to the said Ag-based alloy. If the total amount of the thus selected element is controlled within 0.1 ~ 3 atomic %, excellent endurance (especially, chemical stability) can be realized and exhibits a controlled general appearance and high reflectivity can be maintained.

This invention also includes Ag-based sputtering target for the photo information memory medium used for obtaining the Ag-based alloy film; such sputtering target includes Ag-based alloy sputtering target containing 0.05 ~ 4.5 atomic % Bi, or Ag-based alloy sputtering target containing 0.005 ~ 0.40 atomic % Sb. Similarly as the aforementioned Ag-based alloy thin film, it is preferable, in addition to Bi and/or Sb, to add at least one element selected from an element group comprising of rare earth elements, or at least one element chosen from an element group comprising of Cu, Au, Rh, Pd and Pt.

It is also a preferable embodiment of this invention to provide the photo information memory medium which is furnished by the reflective film or semi-transparent reflective film made of the said Ag-based alloys.

[Embodiments]

The inventers have continuously and diligently investigated to develop new Ag-based alloy reflective film or semi-transparent reflective film useful for the photo information memory medium possessing high thermal conductivity, high reflectivity, and high endurance. As a result, Ag-based alloy with 0.005 ~ 0.40 atomic % of Bi and/or Sb as the total amount was developed and found that this newly developed Ag-based alloy exhibited equivalent high reflectivity and high thermal conductivity as the pure Ag, and better high endurance than pure Ag. In the following, detailed information of this invention will be described.

According to this invention, the Ag-based alloy reflective film for the photo information memory medium contains total amount of 0.005 ~ 0.40 atomic % of Bi and/or Sb as essential alloying element. Reflective film as well as semi-transparent reflective film made of such newly developed Ag-based alloy exhibits equivalent high thermal conductivity and high reflectivity as pure Ag and better endurance characteristics (both thermal and chemical stabilities) than pure Ag.

Since pure Ag thin film which was film-formed by the sputtering method normally contains many crystalline defects (pores, dislocations, grain boundaries), Ag atoms can easily diffuse through these crystalline defects. As a result, when pure Ag thin film is exposed to high temperature high humidity environment, Ag atoms diffuse and aggregated at many sites to cause surface roughening and grain growth. Under the environment containing chlorine ion, similarly Ag atoms tend to diffuse and condense. Surface alternations of such thin films caused by the localized condensation reduce the reflectivity and deteriorate remarkably the memory-reproduction characteristics of the photo discs. Particularly with the extremely thin semi-transparent reflective film used for DVD-ROM, condensation affects adversely the reflectivity, and deteriorates the reproduction performance and capability of the photo disc.

To solve the aforementioned drawback associated with the conventional type of photo discs, adding alloying elements (noble metal such as Au, Pd, Pt etc. or rare earth elements such as Y etc.) to Ag-base has been proposed.

However, when noble metals (such as Au, Pd, or Pt etc.) are alloyed to Ag-base, the condensation (or aggregation) of Ag atoms due to an existence of chlorine ions can be controlled, but condensation of Ag atoms under high temperature and humidity can not be controlled. Moreover, alloying Y element to Ag-base can control the Ag atoms condensation under the high temperature and humidity atmosphere, but Ag atoms condensation under the presence of chlorine ion can not be controlled. Therefore, either one of proposed alloy systems can not control Ag atoms in both high temperature high humid atmosphere and chlorine ion containing environment.

However, according to the present invention, by adding Bi and/or Sb within the total amount of more than 0.005 atomic % to Ag-base, Ag atoms condensation under the high temperature and high humidity and under the existence of chlorine environment can be simultaneously controlled. Moreover, it was found that, by increasing adding amount of these alloying elements of Bi and/or Sb, the anti-condensation effect was enhanced. However, adding the said alloying elements to Ag-base decreased thermal conductivity and reflectivity, and this reducing trendency becomes more remarkable by increasing adding amount. As a result, alloying the Ag-base with Bi and/or Sb reduced both thermal conductivity and reflectivity.

The total adding amount of the said Bi and/or Sb can increase up to 3 atomic % in order to maintain the high reflectivity against the blue-violet laser ray which is used for the next generation photo discs. However, if they exceeds 0.40 atomic %, the high thermal conductivity which is required for the high-speed DVD or the next generation photo disc can not be achieved, so that it becomes hard to maintain the both high thermal conductivity and high reflectivity. Accordingly, the total adding amount should be set forth 0.40 atomic % as most. On the other hand, if adding amount is less than 0.005 atomic %, the alloying effect for controlling the anti-condensation can not be achieved. Preferably, it should be more than 0.01 atomic % and less than 0.3 atomic %, more preferably it should be more than 0.05 atomic % and less than 0.2 atomic %. Moreover,

when the productivity of sputtering targets is concerned, it is preferable to select Bi element due to its ease handling property.

This invention also discloses another alloying elements of rare earth elements for enhancing the endurance and the thermal stability instead of adding Bi and/or Sb to Ag-base alloy. These rare earth elements can control further the localized condensation of Ag atoms to improve the endurance. As rare earth elements, it is prefer to select Nd and/or Y. Preferably the total amount of Nd and/or Y element should be more than 0.01 atomic % and less than 2 atomic %. If it is less than 0.1 atomic %, the aforementioned effects can not be achieved. If it exceeds 2 atomic %, the high thermal conductivity can not be obtained. The most preferable upper limit would be 1 atomic %, more preferably it should be 0.5 atomic %.

For further improvement of endurance (particularly, chemical stability), at least one element selected from the element groups comprising of Cu, Au, Rh, Pd, and Pt may be added to Ag-based alloy containing Bi and/or Sb. These additional elements (Cu, Au, Rh, Pd, and Pt) are believed to control the Ag atoms segregation under the influence of chlorine ions, resulting in further improvement of endurance. It is preferable to add as the total amount more than 0.1 atomic % and less than 3 atomic %. More preferably, it should be 2 atomic % at most.

Moreover, in addition to the said elements, it is effective to add Mg, Ti, and Zn for further improvement of chemical stability. Although the alloying effect of these Mg, Ti, and Zn is not equivalent to that of Au, Rh, Pd, or Pt, it would be effective to help the cost down of the photo discs since their raw price is relatively cheap. Since if the adding amount of Mg, Ti and Zn increases, they might reduce the thermal conductivity and reflectivity, it should be set forth to have an upper limit of 3 atomic % as the total adding amount. Although the above argument was made for only one element application, the similar alloying effect can be realized if more than two elements are multi-alloyed. Alloying effect of Nd and/or Y as rare earth elements and alloying effect of one element from a group of Cu, Au, Rh, Pd, and Pt exhibits an identical alloying effect which can be realized with Ag-based alloy containing B and/or Sb. And these allying effects can not be found with pure Ag.

As disclosed in the Tokkai 2001-184725, it was known that Ag-based alloy added with one element chosen from the element group comprising of Al, Au, Cu, Co, Ni, Ti, V, Mo, Mn, Pt, Si, Nb, Fe, Ta, Hf, Ga, Pd, Bi, In, W, and Zr within a 0.5 ~ 5 atomic % increased the corrosion resistance. However, element like Al, Au, Cu, Pt, and Pd does not show the beneficial alloying effect to control the Ag atoms segregation when Ag thin film was held at high temperature. Hence, these alloying elements did not improve the endurance improvement (thermal stability), unlikely the main objective of this invention. Moreover, if Bi is added with more than 0.5 atomic %, it might cause to reduce the thermal conductivity, so that this idea should be eliminated. Furthermore, the Tokkai 2002-92959 disclosed Ag-based alloy with Cu with 4 ~ 15 mass % and Al, Zn, Cd, Sn, Sb, and Ir with more than 0.5 mass % to enhance the chemical stability. With Cu, Al, Zn, Cd, Sn, and Ir alloying, Ag atom segregation can not be controlled. Moreover, if Sb is added more than 0.5 mass % (or 0.44 atomic %), it causes to reduce the thermal conductivity of original value of Ag element. These prior art Ag-based alloys should be clearly distinguished from those which are herein disclosed according to this invention.

Ag-based alloy reflective film or Ag-based alloy semi-transparent reflective film useful for the photo information memory medium, according to the present invention, can be fabricated through vacuum deposition method, ion pray coating method or sputtering method of Ag-based alloy. Among these methods, the sputtering method can be recommended. Ag-based alloy reflective film or Ag-based alloy semi-transparent reflective film fabricated through the sputtering technique possesses several advantages over such films produced by other techniques. They can include that (1) excellent homogeneities of alloying elements included in Ag-based alloy and film thickness, (2) high level of properties (high thermal conductivity, high reflectivity, high endurance) as a reflective film, and (3) production of photo discs with high reliability with high performance.

In this invention, the Ag-based alloy reflective film for photo information memory medium implies a reflective film of single layer for memory on only one side of disc, and a thin film used as an outer reflective film of multi-later structure. Such film possesses a penetrating power of almost 0% and a reflectivity of about 45% or more, depending on the disc structures. As to the film thickness, although it should be appropriately selected

within satisfactory ranges for reflectivity and penetrating power, it can be in a range of 50 ~ 200 nm for standard value.

In this invention, the semi-transparent film implies a film used as reflective film for a medium which performs more than double-layer multi-memory on one side of the disc. The penetration power is controlled in a range of 60 ~ 72%, and 18 ~ 30% for the reflectivity, again depending on the disc structures. The film thickness is about 5 ~ 20 nm as a standard reference, although the appropriate film thickness should be determined according to the reflectivity and penetration power.

Ag-based alloy sputtering target used for the photo information memory medium, according to the invention, can be manufactured by either melting/casting method, powder metallurgy technique, or spray forming method. Among them, the melting/casting method can be recommended. Ag-based alloy sputtering target which is manufactured by the vacuum melting and casting method contains less amount of impurities such as nitrogen or oxygen when compared to those produced by the other methods. Reflective film or semi-transparent reflective film which is fabricated using sputtering target possesses high characteristics (such as high thermal conductivity, high reflectivity, and high endurance), so that photo discs with higher reliability and performance can be produced.

Although, according to this invention, the reflective film and semi-transparent reflective film should contain essential alloying element of Bi and/or Sb within a range of 0.005 ~ 0.40 atomic %, it is necessary to include Bi in a range of 0.05 ~ 4.5 atomic % in the sputtering target in order to maintain the Bi content as described in the above.

In ordinary alloying systems such as Ag-Cu alloy, Ag-noble metal alloy, or Ag-rare earth element alloy, compositions in sputtering target are very similar to those in fabricated thin film. On the contrary, Bi content in formed thin film is normally reduced down to several % to several 10% than those in Ag-based alloy sputtering target.

The main reasons for this decease in contents are (1) a large discrepancy in melting points between Ag and Bi, and due to high vapor pressure of Bi, Bi can be re-evaporated from the base substrate during sputtering, (2) due to a large sputter rate of Ag than that of Bi, Bi is hardly be sputtered, and (3) since Bi is much easier oxidized than Ag, only Bi is

oxidized on the sputtering target surface. Because of these reasons, it is speculated that Bi content in formed thin film is lower than that in sputtering target.

Therefore, it is necessary to increase the Bi content in the sputtering target more than the final value of Bi content in reflective film or semi-transparent reflective film. For example, in order to obtain the reflective film or semi-transparent reflective film having Bi content of 0.005 ~ 0.40 atomic %, Bi content should be more than 0.05 atomic % and les than 4.5 atomic % in the sputtering target. Preferably, it can be more than 0.1 atomic % and less than 3.6 atomic %.

The aforementioned phenomena of Bi dilution can not be observed in Ag-Sb alloys, Ag-rare earth element alloys, or other Ag-based alloys. With these alloying systems, chemical compositions of the sputtering target and those of formed film are normally coincident. Hence, even in this invention, in order to forming a film using the sputtering target if it does not contain Bi element, the sputtering target should be made containing the same level of each element's content.

The photo information memory medium of this invention is sufficient good enough if it is furnished with Ag-based alloy reflective film or semi-transparent reflective film of this invention. Other structural details of this photo information memory medium are not needed to be specified, and all possible prior art structures available in the photo information memory medium field can be applied. For example, the photo information memory media of this invention which provides a polycarbonate transparent base substrate on whose one side was furnished with the reflective film or semi-transparent reflective film comprising of Ag-based alloy possess high reflectivity, high thermal conductivity, and high endurance. Therefore, it can be used not only as a photo information memory medium for read-only type, write-add type, or overwrite editable disc, but also be suitable for the high-speed DVD and the next generation discs.

[Examples]

In the followings, several experiments conducted for this invention will be described. The experiments are not necessarily limited to the scope of this invention, and the invention is not confined to the details as set forth. The application is intended to cover modifications and changes as may come within the scope of the claims.

[Production of Ag-based alloy thin film]

Using a double-target on which chips of various alloying elements are provided on pure Ag sputtering target, the following reflective film (film thickness of 100nm) or semi-transparent reflective film (film thickness of 15nm) was formed on polycarbonate base substrate (diameter: 50mm, thickness: 1mm) through the DC magnetron sputtering method. The sample films were as follows: Pure Ag (sample No. 1), Ag-Bi alloy (sample Nos. 2 – 5), Ag-Sb alloy (sample Nos. 6 – 9), Ag-Bi-Nd alloy (sample Nos. 10 -14), Ag-Bi-Y alloy (sample Nos. 15 – 19), Ag-Sb-Nd alloy (sample Nos. 20 – 24), Ag-Sb-Y alloy (sample Nos. 25 – 29), Ag-Bi-Cu alloy (sample Nos. 30 – 34), Ag-Bi-Au alloy (sample Nos. 35 – 39), Ag-Sb-Cu alloy (sample Nos. 40 – 44), Ag-Sb-Au alloy (sample Nos. 45 – 49), Ag-Bi-Nd-Cu alloy (sample No. 50), Ag-Bi-Nd-Au alloy (sample No. 51), Ag-Bi-Y-Cu alloy (sample No. 52), Ag-Bi-Y-Au alloy (sample No. 53), Ag-Sb-Nd-Cu alloy (sample No. 54), Ag-Sb-Nd-Au alloy (sample No. 55), Ag-Sb-Y-Cu alloy (sample No. 56), Ag-Sb-Y-Au alloy (sample No. 57), Ag-Si alloy (sample No. 58), and Ag-Sn alloy (sample No. 59). Chemical compositions of these formed Ag-based alloy film were analyzed by the ICP (inductively coupled plasma) mass spectroscopy.

Characteristics of reflective film (film thickness: 100nm) or semi-transparent reflective film (film thickness: 15nm) were investigated in terms of the thermal conductivity, reflectivity, and endurance. The endurance evaluation for the thermal stability was examined the changes in reflectivity and surface roughness (averaged roughness) before and after the high temperature and high humidity tests. The endurance evaluation of the chemical stability was conducted on the changes in general appearance before and after the salt water immersion tests.

[Experiment 1: Thermal conductivity measurement]

The thermal conductivity of films (with thickness of 100nm) prepared by the aforementioned method was measured as follows; the sheet resistance Rs was firstly measured by the four-needle method using HIOKI 3226 mΩ Hi Tester, the film thickness t was measured by TENCOR INSTRUMENTS alpha-step 250, and the electric resistance ρ (= sheet resistance Rs x film thickness t) was calculated. Based on the thus calculated ρ,

the thermal conductivity κ was obtained (= 2.51 x absolute temperature T/electric resistance ρ) at absolute temperature 300K (=27°C) according to the Wiedemann-Franz's law. For evaluation purpose, if the film exhibits more than 80% (in other words, 256W/(mxK)) of the thermal conductivity of pure Ag (320W/(mxK)), the film was evaluated as the film having the high conductivity film. Results are shown in Tables 1 and 2.

As clearly shown in Tables 1 and 2, pure Ag film (sample No. 1), Ag-Si alloy (sample No. 58), and Ag-based alloy samples which satisfies the specifications set forth in this application (Nos. 2 – 4, 6 – 8, 10 – 13, 15 – 18, 20 – 23, 25 – 28, 30 – 33, 35 – 38, 40 – 43, 45 – 48, 50 – 57) were evaluated as films with high conductivity. On the other hand, Ag-based alloy samples Nos. 5, 9, 14, 19, 24, 29, 34, 39, 44, and 49 did not show high conductivity due to excessive alloying element content. High thermal conductivity was not also obtained with Ag-Sn alloy film (sample No. 59). Alloying effect of Rh, Pd or Pt was similar to that of Cu and Au elements.

Table 1. Results of thermal conductivity

sample number	composition	Thermal conductivity [W/(mK)]	High thermal conductivity
1	Pure Ag	320	O
2	Ag-0.005at%Bi alloy	319	O
3	Ag-0.2at%Bi alloy	296	O
4	Ag-0.4at%Bi alloy	271	O
5	Ag-0.6at%Bi alloy	247	X
6	Ag-0.005at%Sb alloy	319	O
7	Ag-0.2at%Sb alloy	292	O
8	Ag-0.4at%Sb alloy	264	O
9	Ag-0.6at%Sb alloy	236	X
10	Ag-0.2at%Bi-0.01at%Nd alloy	296	O
11	Ag-0.2at%Bi-0.1at%Nd alloy	294	O
12	Ag-0.2at%Bi-0.5at%Nd alloy	287	O
13	Ag-0.2at%Bi-2at%Nd alloy	260	O
14	Ag-0.2at%Bi-3at%Nd alloy	242	X
15	Ag-0.2at%Bi-0.01at%Y alloy	296	O
16	Ag-0.2at%Bi-0.1at%Y alloy	294	O
17	Ag-0.2at%Bi-0.5at%Y alloy	288	O
18	Ag-0.2at%Bi-2at%Y alloy	262	O
19	Ag-0.2at%Bi-3at%Y alloy	245	X
20	Ag-0.2at%Sb-0.01at%Nd alloy	292	O
21	Ag-0.2at%Sb-0.1at%Nd alloy	290	O
22	Ag-0.2at%Sb-0.5at%Nd alloy	283	O
23	Ag-0.2at%Sb-2at%Nd alloy	256	O
24	Ag-0.2at%Sb-3at%Nd alloy	238	X
25	Ag-0.2at%Sb-0.01at%Y alloy	292	O
26	Ag-0.2at%Sb-0.1at%Y alloy	290	O
27	Ag-0.2at%Sb-0.5at%Y alloy	284	O
28	Ag-0.2at%Sb-2at%Y alloy	258	O
29	Ag-0.2at%Sb-3at%Y alloy	241	X

Table 2. Results of thermal conductivity

sample number	composition	Thermal conductivity [W/(mK)]	High thermal conductivity
1	Pure Ag	320	O
30	Ag-0.2at%Bi-0.01at%Cu alloy	296	O
31	Ag-0.2at%Bi-0.1at%Cu alloy	295	O
32	Ag-0.2a%Bi-0.5at%Cu alloy	290	O
33	Ag-0.2a%Bi-3at%Cu alloy	260	O
34	Ag-0.2a%Bi-4at%Cu alloy	248	X
35	Ag-0.2at%Bi-0.01at%Au alloy	296	O
36	Ag-0.2at%Bi-0.5at%Au alloy	295	O
37	Ag-0.2at%Bi-0.5at%Au alloy	290	O
38	Ag-0.2at%Bi-3at%Au alloy	262	O
39	Ag-0.2at%Bi-4at%Au alloy	251	X
40	Ag-0.2at%Sb-0.01at%Cu alloy	292	O
41	Ag-0.2at%Sb-0.1at%Cu alloy	291	O
42	Ag-0.2at%Sb-0.5at%Cu alloy	286	O
43	Ag-0.2at%Sb-3at%Cu alloy	256	O
44	Ag-0.2at%Sb-4at%Cu alloy	244	X
45	Ag-0.2at%Sb-0.01at%Au alloy	292	O
46	Ag-0.2at%Sb-0.1at%Au alloy	291	O
47	Ag-0.2at%Sb-0.5at%Au alloy	286	O
48	Ag-0.2at%Sb-3at%Au alloy	258	O
49	Ag-0.2at%Sb-4at%Au alloy	247	X
50	Ag-0.2at%Bi-0.5at%Nd-0.5at%Cu alloy	281	O
51	Ag-0.2at%Bi-0.5at%Nd-0.5a5%Au alloy	281	O
52	Ag-0.2at%Bi-0.5at%Y-0.5at%Cu alloy	282	O
53	Ag-0.2at%Bi-0.5at%Y-0.5at%Au alloy	282	O
54	Ag-0.2at%Sb-0.5at%Nd-0.5a5%Cu alloy	277	O
55	Ag-0.2at%Sb-0.5at%Nd-0.5a5%Au alloy	277	O
56	Ag-0.2at%Sb-0.5at%Y-0.5a5Cu alloy	278	O
57	Ag-0.2at%Sb-0.5at%Y-0.5a5%Au alloy	278	O
58	Ag-0.2at%Si alloy	265	O
59	Ag-0.2at%Sn alloy	248	X

[Experiment 2: Reflectivity measurement]

The reflectivity of the film with thickness of 100 nm against the visible rays (wave length: 400 – 800nm) was measured using Nihon Kagaku Engineering Polar Kerr Scope NEO ARK MODEL BH-810. For evaluation, with reference points of 90.8% (wavelength: 405 nm) and 92.5% (wavelength: 650 nm) of pure Ag, if the film exhibits more than 80% (wavelength: 405 nm) or more than 88% (wavelength: 650 nm), the film was evaluated as a film with high reflectivity. The wave length of 405 nm is a wave length of the laser light used for the next generation light disc and the wave length of 605 nm is the wave length of laser ray used for DVD.

Tables 3 and 4 show results of test. As clearly shown in Tables 3 and 4, pure Ag film(sample No. 1), Ag-Si alloy (sample No. 58), Ag-Sn alloy (sample No. 59), and Ag-based alloy samples which satisfies the specifications set forth in this application (Nos. 2 – 4, 6 – 8, 10 – 13, 15 – 18, 20 – 23, 25 – 28, 30 – 33, 35 – 38, 40 – 43, 45 – 48, 50 – 57) were evaluated as films with high thermal reflectivity. On the contrary, due to excessive alloying element contents, Ag-based alloy sample Nos. 5, 9, 14, 19, 24, 34, 39, 44, and 49 did not exhibit the satisfactory level of thermal reflectivity. The alloying effect of Rh, Pd, and Pt is similar to those of Cu or Au.

Table 3. Results of reflectivity

sample number	composition	Reflectivity (%) against pure Ag		High reflectivity
		Wave length 405nm	Wave length 650nm	
1	Pure Ag	90.8	92.5	O
2	Ag-0.005at%Bi alloy	90.7	92.5	O
3	Ag-0.2at%Bi alloy	86.2	90.8	O
4	Ag-0.4at%Bi alloy	81.6	89.1	O
5	Ag-0.6at%Bi alloy	77.0	87.4	X
6	Ag-0.005at%Sb alloy	90.7	92.5	O
7	Ag-0.2at%Sb alloy	86.1	90.7	O
8	Ag-0.4at%Sb alloy	81.4	88.9	O
9	Ag-0.6at%Sb alloy	76.7	87.1	X
10	Ag-0.2at%Bi-0.01at%Nd alloy	86.2	90.8	O
11	Ag-0.2at%Bi-0.1at%Nd alloy	85.9	90.7	O
12	Ag-0.2at%Bi-0.5at%Nd alloy	84.8	90.3	O
13	Ag-0.2at%Bi-2at%Nd alloy	80.7	88.6	O
14	Ag-0.2at%Bi-3at%Nd alloy	78.0	87.5	X
15	Ag-0.2at%Bi-0.01at%Y alloy	86.2	90.8	O
16	Ag-0.2at%Bi-0.1at%Y alloy	85.9	90.7	O
17	Ag-0.2at%Bi-0.5at%Y alloy	84.7	90.2	O
18	Ag-0.2at%Bi-2at%Y alloy	80.3	88.4	O
19	Ag-0.2at%Bi-3at%Y alloy	77.4	87.2	X
20	Ag-0.2at%Sb-0.01at%Nd alloy	86.1	90.7	O
21	Ag-0.2at%Sb-0.1at%Nd alloy	85.8	90.6	O
22	Ag-0.2at%Sb-0.5at%Nd alloy	84.7	90.2	O
23	Ag-0.2at%Sb-2at%Nd alloy	80.6	88.5	O
24	Ag-0.2at%Sb-3at%Nd alloy	77.9	87.4	X
25	Ag-0.2at%Sb-0.01at%Y alloy	86.1	90.7	O
26	Ag-0.2at%Sb-0.1at%Y alloy	85.8	90.6	O
27	Ag-0.2at%Sb-0.5at%Y alloy	84.6	90.1	O
28	Ag-0.2at%Sb-2at%Y alloy	80.2	88.3	O
29	Ag-0.2at%Sb-3at%Y alloy	77.3	87.1	X

Table 4. Results of reflectivity

sample number	composition	Reflectivity (%)		Hi ref.
		405nm	650nm	
1	Pure Ag	90.8	92.5	O
30	Ag-0.2at%Bi-0.01at%Cu alloy	86.2	90.8	O
31	Ag-0.2at%Bi-0.1at%Cu alloy	86.0	90.7	O
32	Ag-0.2a%Bi-0.5at%Cu alloy	85.3	90.4	O
33	Ag-0.2a%Bi-3at%Cu alloy	81.0	88.3	O
34	Ag-0.2a%Bi-4at%Cu alloy	79.3	87.5	X
35	Ag-0.2at%Bi-0.01at%Au alloy	86.2	90.8	O
36	Ag-0.2at%Bi-0.5at%Au alloy	86.0	90.7	O
37	Ag-0.2at%Bi-0.5at%Au alloy	85.4	90.4	O
38	Ag-0.2at%Bi-3at%Au alloy	81.5	88.5	O
39	Ag-0.2at%Bi-4at%Au alloy	79.9	87.7	X
40	Ag-0.2at%Sb-0.01at%Cu alloy	86.1	90.7	O
41	Ag-0.2at%Sb-0.1at%Cu alloy	85.9	90.6	O
42	Ag-0.2at%Sb-0.5at%Cu alloy	85.2	90.3	O
43	Ag-0.2at%Sb-3at%Cu alloy	80.9	88.2	O
44	Ag-0.2at%Sb-4at%Cu alloy	79.2	87.4	X
45	Ag-0.2at%Sb-0.01at%Au alloy	86.1	90.7	O
46	Ag-0.2at%Sb-0.1at%Au alloy	85.9	90.6	O
47	Ag-0.2at%Sb-0.5at%Au alloy	85.3	90.3	O
48	Ag-0.2at%Sb-3at%Au alloy	81.4	88.4	O
49	Ag-0.2at%Sb-4at%Au alloy	79.8	87.6	X
50	Ag-0.2at%Bi-0.5at%Nd-0.5at%Cu alloy	84.0	89.8	O
51	Ag-0.2at%Bi-0.5at%Nd-0.5a5%Au alloy	84.0	89.9	O
52	Ag-0.2at%Bi-0.5at%Y-0.5at%Cu alloy	83.9	89.8	O
53	Ag-0.2at%Bi-0.5at%Y-0.5at%Au alloy	83.9	89.8	O
54	Ag-0.2at%Sb-0.5at%Nd-0.5a5%Cu alloy	83.9	89.7	O
55	Ag-0.2at%Sb-0.5at%Nd-0.5a5%Au alloy	83.9	89.8	O
56	Ag-0.2at%Sb-0.5at%Y-0.5a5Cu alloy	83.8	89.7	O
57	Ag-0.2at%Sb-0.5at%Y-0.5a5%Au alloy	83.8	89.7	O
58	Ag-0.2at%Si alloy	85.5	90.3	O
59	Ag-0.2at%Sn alloy	85.0	89.9	O

[Experiment 3: Endurance Test 1: Thermal Stability Evaluation]

Same samples used for the reflectivity measurements with film thickness of 100 nm were subjected to the high temperature and high humidity tests (temperature 80°C, humidity 90%RH, for 48 hours). The changes in reflectivity before and after the tests were measured. If the absolute value of reflectivity changes before and after the tests is less than 5% (wave length 405 nm) or less than 1% (wave length 650 nm), the film was evaluated as a film with high endurance. Results are shown in Tables 5 and 6.

As clearly seen from Tables 5 and 6, Ag-based alloy sample Nos. 2 – 57 which satisfy the specifications of this invention exhibited high endurance. On the other hand, pure Ag (sample No. 1), Ag-Si alloy (sample No. 58), and Ag-Sn alloy (sample No. 59) did not show the satisfactory level of endurance. The alloying effect of Rh, Pd, or Pt is similar to that of Cu or Au.

Table 5. Results of endurance (thermal stability) evaluation

sample number	composition	Change in reflectivity (%) b/w before and after high temp high humid tests		endurance
		Wave length 405nm	Wave length 650nm	
1	Pure Ag	-27.3	-3.0	X
2	Ag-0.005at%Bi alloy	-1.4	-0.8	O
3	Ag-0.2at%Bi alloy	-0.7	-0.3	O
4	Ag-0.4at%Bi alloy	-0.5	-0.2	O
5	Ag-0.6at%Bi alloy	-0.3	-0.1	O
6	Ag-0.005at%Sb alloy	-1.6	-0.9	O
7	Ag-0.2at%Sb alloy	-0.8	-0.4	O
8	Ag-0.4at%Sb alloy	-0.6	-0.3	O
9	Ag-0.6at%Sb alloy	-0.4	-0.2	O
10	Ag-0.2at%Bi-0.01at%Nd alloy	-0.6	-0.2	O
11	Ag-0.2at%Bi-0.1at%Nd alloy	-0.5	-0.1	O
12	Ag-0.2at%Bi-0.5at%Nd alloy	-0.3	-0.1	O
13	Ag-0.2at%Bi-2at%Nd alloy	0.0	0.0	O
14	Ag-0.2at%Bi-3at%Nd alloy	0.0	0.0	O
15	Ag-0.2at%Bi-0.01at%Y alloy	-0.6	-0.2	O
16	Ag-0.2at%Bi-0.1at%Y alloy	-0.5	-0.1	O
17	Ag-0.2at%Bi-0.5at%Y alloy	-0.4	-0.1	O
18	Ag-0.2at%Bi-2at%Y alloy	0.0	0.0	O
19	Ag-0.2at%Bi-3at%Y alloy	0.0	0.0	O
20	Ag-0.2at%Sb-0.01at%Nd alloy	-0.7	-0.3	O
21	Ag-0.2at%Sb-0.1at%Nd alloy	-0.6	-0.2	O
22	Ag-0.2at%Sb-0.5at%Nd alloy	-0.4	-0.2	O
23	Ag-0.2at%Sb-2at%Nd alloy	0.0	0.0	O
24	Ag-0.2at%Sb-3at%Nd alloy	0.0	0.0	O
25	Ag-0.2at%Sb-0.01at%Y alloy	-0.7	-0.3	O
26	Ag-0.2at%Sb-0.1at%Y alloy	-0.6	-0.2	O
27	Ag-0.2at%Sb-0.5at%Y alloy	-0.5	-0.2	O
28	Ag-0.2at%Sb-2at%Y alloy	0.0	0.0	O
29	Ag-0.2at%Sb-3at%Y alloy	0.0	0.0	O

Table 6. Results of endurance (thermal stability) evaluation

sample number	composition	Change in reflectivity (%) b/w before and after high temp high humid tests		endurance
		405nm	650nm	
1	Pure Ag	-27.3	-3.0	X
30	Ag-0.2at%Bi-0.01at%Cu alloy	-0.6	-0.2	O
31	Ag-0.2at%Bi-0.1at%Cu alloy	-0.5	-0.1	O
32	Ag-0.2a%Bi-0.5at%Cu alloy	-0.4	-0.1	O
33	Ag-0.2a%Bi-3at%Cu alloy	0.0	0.0	O
34	Ag-0.2a%Bi-4at%Cu alloy	0.0	0.0	O
35	Ag-0.2at%Bi-0.01at%Au alloy	-0.6	-0.2	O
36	Ag-0.2at%Bi-0.5at%Au alloy	-0.5	-0.1	O
37	Ag-0.2at%Bi-0.5at%Au alloy	-0.4	-0.1	O
38	Ag-0.2at%Bi-3at%Au alloy	0.0	0.0	O
39	Ag-0.2at%Bi-4at%Au alloy	0.0	0.0	O
40	Ag-0.2at%Sb-0.01at%Cu alloy	-0.7	-0.3	O
41	Ag-0.2at%Sb-0.1at%Cu alloy	-0.6	-0.2	O
42	Ag-0.2at%Sb-0.5at%Cu alloy	-0.4	-0.1	O
43	Ag-0.2at%Sb-3at%Cu alloy	0.0	0.0	O
44	Ag-0.2at%Sb-4at%Cu alloy	0.0	0.0	O
45	Ag-0.2at%Sb-0.01at%Au alloy	-0.7	-0.3	O
46	Ag-0.2at%Sb-0.1at%Au alloy	-0.5	-0.2	O
47	Ag-0.2at%Sb-0.5at%Au alloy	-0.3	-0.1	O
48	Ag-0.2at%Sb-3at%Au alloy	0.0	0.0	O
49	Ag-0.2at%Sb-4at%Au alloy	0.0	0.0	O
50	Ag-0.2at%Bi-0.5at%Nd-0.5at%Cu alloy	0.0	0.0	O
51	Ag-0.2at%Bi-0.5at%Nd-0.5a5%Au alloy	0.0	0.0	O
52	Ag-0.2at%Bi-0.5at%Y-0.5at%Cu alloy	0.0	0.0	O
53	Ag-0.2at%Bi-0.5at%Y-0.5at%Au alloy	0.0	0.0	O
54	Ag-0.2at%Sb-0.5at%Nd-0.5a5%Cu alloy	0.0	0.0	O
55	Ag-0.2at%Sb-0.5at%Nd-0.5a5%Au alloy	0.0	0.0	O
56	Ag-0.2at%Sb-0.5at%Y-0.5a5Cu alloy	0.0	0.0	O
57	Ag-0.2at%Sb-0.5at%Y-0.5a5%Au alloy	0.0	0.0	O
58	Ag-0.2at%Si alloy	-19.9	-2.1	X
59	Ag-0.2at%Sn alloy	-18.4	-1.8	X

[Experiment 4: Endurance Test 2: Chemical Stability Evaluation]

Films (film thickness of 15 nm) fabricated according to the invention were subjected to the salt water immersion tests (concentration of NaCl: 0.05mol/L, salt water temperature: 20°C, immersion time: 5 min.). The general appearance changes before and after the immersion tests were performed. If no remarkable changes in appearances such as discoloration or peeling-off were noticed, the film was evaluated as a film with high endurance.

From Tables 7 and 8, Ag-based alloy sample Nos. 2 – 57 which were fabricated according to the specifications of the invention showed the satisfactory level of endurance. On the contrary, pure Ag (sample No. 1), Ag-Si alloy (sample No. 58), and Ag-Sn alloy (sample No. 59) did not show high level of endurance. The alloying effect of Rh, Pd, or Pt is similar to that of Cu or Au.

Table 7. Results of changes in general appearance after salt water immersion tests on Ag-system thin film

sample number	Composition	Changes in appearance	Endurance
1	Pure Ag	Yes	X
2	Ag-0.005at%Bi alloy	None	O
3	Ag-0.2at%Bi alloy	None	O
4	Ag-0.4at%Bi alloy	None	O
5	Ag-0.6at%Bi alloy	None	O
6	Ag-0.005at%Sb alloy	None	O
7	Ag-0.2at%Sb alloy	None	O
8	Ag-0.4at%Sb alloy	None	O
9	Ag-0.6at%Sb alloy	None	O
10	Ag-0.2at%Bi-0.01at%Nd alloy	None	O
11	Ag-0.2at%Bi-0.1at%Nd alloy	None	O
12	Ag-0.2at%Bi-0.5at%Nd alloy	None	O
13	Ag-0.2at%Bi-2at%Nd alloy	None	O
14	Ag-0.2at%Bi-3at%Nd alloy	None	O
15	Ag-0.2at%Bi-0.01at%Y alloy	None	O
16	Ag-0.2at%Bi-0.1at%Y alloy	None	O
17	Ag-0.2at%Bi-0.5at%Y alloy	None	O
18	Ag-0.2at%Bi-2at%Y alloy	None	O
19	Ag-0.2at%Bi-3at%Y alloy	None	O
20	Ag-0.2at%Sb-0.01at%Nd alloy	None	O
21	Ag-0.2at%Sb-0.1at%Nd alloy	None	O
22	Ag-0.2at%Sb-0.5at%Nd alloy	None	O
23	Ag-0.2at%Sb-2at%Nd alloy	None	O
24	Ag-0.2at%Sb-3at%Nd alloy	None	O
25	Ag-0.2at%Sb-0.01at%Y alloy	None	O
26	Ag-0.2at%Sb-0.1at%Y alloy	None	O
27	Ag-0.2at%Sb-0.5at%Y alloy	None	O
28	Ag-0.2at%Sb-2at%Y alloy	None	O
29	Ag-0.2at%Sb-3at%Y alloy	None	O

Table 8. Results of changes in general appearance after salt water immersion tests on Ag-system thin film

sample number	Composition	Changes in appearance	Endurance
1	Pure Ag	Yes	X
30	Ag-0.2at%Bi-0.01at%Cu alloy	None	O
31	Ag-0.2at%Bi-0.1at%Cu alloy	None	O
32	Ag-0.2a%Bi-0.5at%Cu alloy	None	O
33	Ag-0.2a%Bi-3at%Cu alloy	None	O
34	Ag-0.2a%Bi-4at%Cu alloy	None	O
35	Ag-0.2at%Bi-0.01at%Au alloy	None	O
36	Ag-0.2at%Bi-0.5at%Au alloy	None	O
37	Ag-0.2at%Bi-0.5at%Au alloy	None	O
38	Ag-0.2at%Bi-3at%Au alloy	None	O
39	Ag-0.2at%Bi-4at%Au alloy	None	O
40	Ag-0.2at%Sb-0.01at%Cu alloy	None	O
41	Ag-0.2at%Sb-0.1at%Cu alloy	None	O
42	Ag-0.2at%Sb-0.5at%Cu alloy	None	O
43	Ag-0.2at%Sb-3at%Cu alloy	None	O
44	Ag-0.2at%Sb-4at%Cu alloy	None	O
45	Ag-0.2at%Sb-0.01at%Au alloy	None	O
46	Ag-0.2at%Sb-0.1at%Au alloy	None	O
47	Ag-0.2at%Sb-0.5at%Au alloy	None	O
48	Ag-0.2at%Sb-3at%Au alloy	None	O
49	Ag-0.2at%Sb-4at%Au alloy	None	O
50	Ag-0.2at%Bi-0.5at%Nd-0.5at%Cu alloy	None	O
51	Ag-0.2at%Bi-0.5at%Nd-0.5a5%Au alloy	None	O
52	Ag-0.2at%Bi-0.5at%Y-0.5at%Cu alloy	None	O
53	Ag-0.2at%Bi-0.5at%Y-0.5at%Au alloy	None	O
54	Ag-0.2at%Sb-0.5at%Nd-0.5a5%Cu alloy	None	O
55	Ag-0.2at%Sb-0.5at%Nd-0.5a5%Au alloy	None	O
56	Ag-0.2at%Sb-0.5at%Y-0.5a5Cu alloy	None	O
57	Ag-0.2at%Sb-0.5at%Y-0.5a5%Au alloy	None	O
58	Ag-0.2at%Si alloy	Yes	X
59	Ag-0.2at%Sn alloy	Yes	X

[Experiment 5: Endurance Test 3: Thermal Stability Evaluation]

Films fabricated with film thickness of 100 nm were subjected to the morphological observation as well as surface roughness measurements (average roughness: Ra) under the AFM mode (Atomic Force Microscope), using the Digital Instruments Nanoscope IIIa Scanning Probe Microscopy. Films which were examined under AFM mode measurements were further subjected to the high temperature and high humidity tests (temperature: 80°C, humidity: 90%RH, for 48 hours), followed by the surface morphological observation as well as surface roughness measurements (average roughness; Ra). If the film shows the average roughness of less than 1% for both before and after the high temperature and high humidity tests, the film was evaluated to be a film with high endurance. Tables 9 and 10 list the test results.

As seen clearly from Tables 9 and 10, Ag-based alloy sample Nos. 2 – 57 which were fabricated according to the specification set forth in this invention showed the high endurance. On the contrary, pure Ag (sample No. 1), Ag-Si alloy (sample No. 58) and Ag-Sn alloy (sample No.59) did not satisfactory level of endurance. The alloying effect of Rh, Pd,or Pt was similar to that of Cu or Au.

Table 9. Average roughness of Ag-system thin film before and after the high temperature and high humidity tests

sample number	composition	Average roughness [nm]		endurance
		Before test	After test	
1	Pure Ag	4.18	7.33	X
2	Ag-0.005at%Bi alloy	0.63	0.93	O
3	Ag-0.2at%Bi alloy	0.58	0.61	O
4	Ag-0.4at%Bi alloy	0.55	0.58	O
5	Ag-0.6at%Bi alloy	0.52	0.54	O
6	Ag-0.005at%Sb alloy	0.65	0.95	O
7	Ag-0.2at%Sb alloy	0.58	0.63	O
8	Ag-0.4at%Sb alloy	0.56	0.59	O
9	Ag-0.6at%Sb alloy	0.54	0.57	O
10	Ag-0.2at%Bi-0.01at%Nd alloy	0.58	0.60	O
11	Ag-0.2at%Bi-0.1at%Nd alloy	0.55	0.59	O
12	Ag-0.2at%Bi-0.5at%Nd alloy	0.52	0.56	O
13	Ag-0.2at%Bi-2at%Nd alloy	0.45	0.48	O
14	Ag-0.2at%Bi-3at%Nd alloy	0.44	0.48	O
15	Ag-0.2at%Bi-0.01at%Y alloy	0.57	0.60	O
16	Ag-0.2at%Bi-0.1at%Y alloy	0.56	0.59	O
17	Ag-0.2at%Bi-0.5at%Y alloy	0.53	0.58	O
18	Ag-0.2at%Bi-2at%Y alloy	0.47	0.53	O
19	Ag-0.2at%Bi-3at%Y alloy	0.45	0.52	O
20	Ag-0.2at%Sb-0.01at%Nd alloy	0.58	0.62	O
21	Ag-0.2at%Sb-0.1at%Nd alloy	0.56	0.60	O
22	Ag-0.2at%Sb-0.5at%Nd alloy	0.53	0.58	O
23	Ag-0.2at%Sb-2at%Nd alloy	0.47	0.50	O
24	Ag-0.2at%Sb-3at%Nd alloy	0.47	0.49	O
25	Ag-0.2at%Sb-0.01at%Y alloy	0.58	0.63	O
26	Ag-0.2at%Sb-0.1at%Y alloy	0.55	0.61	O
27	Ag-0.2at%Sb-0.5at%Y alloy	0.54	0.60	O
28	Ag-0.2at%Sb-2at%Y alloy	0.46	0.54	O
29	Ag-0.2at%Sb-3at%Y alloy	0.45	0.53	O

Table 10. Average roughness of Ag-system thin film before and after the high temperature and high humidity tests

sample number	Composition	Average roughness [nm]		endurance
		Before test	After test	
1	Pure Ag	4.18	7.33	X
30	Ag-0.2at%Bi-0.01at%Cu alloy	0.59	0.93	O
31	Ag-0.2at%Bi-0.1at%Cu alloy	0.58	0.90	O
32	Ag-0.2a%Bi-0.5at%Cu alloy	0.56	0.86	O
33	Ag-0.2a%Bi-3at%Cu alloy	0.55	0.75	O
34	Ag-0.2a%Bi-4at%Cu alloy	0.54	0.73	O
35	Ag-0.2at%Bi-0.01at%Au alloy	0.59	0.94	O
36	Ag-0.2at%Bi-0.5at%Au alloy	0.57	-.89	O
37	Ag-0.2at%Bi-0.5at%Au alloy	0.56	0.84	O
38	Ag-0.2at%Bi-3at%Au alloy	0.54	0.76	O
39	Ag-0.2at%Bi-4at%Au alloy	0.53	0.75	O
40	Ag-0.2at%Sb-0.01at%Cu alloy	0.59	0.95	O
41	Ag-0.2at%Sb-0.1at%Cu alloy	0.58	0.91	O
42	Ag-0.2at%Sb-0.5at%Cu alloy	0.57	0.88	O
43	Ag-0.2at%Sb-3at%Cu alloy	0.56	0.78	O
44	Ag-0.2at%Sb-4at%Cu alloy	0.54	0.77	O
45	Ag-0.2at%Sb-0.01at%Au alloy	0.58	0.94	O
46	Ag-0.2at%Sb-0.1at%Au alloy	0.58	0.90	O
47	Ag-0.2at%Sb-0.5at%Au alloy	0.57	0.86	O
48	Ag-0.2at%Sb-3at%Au alloy	0.57	0.79	O
49	Ag-0.2at%Sb-4at%Au alloy	0.55	0.77	O
50	Ag-0.2at%Bi-0.5at%Nd-0.5at%Cu alloy	0.50	0.55	O
51	Ag-0.2at%Bi-0.5at%Nd-0.5a5%Au alloy	0.51	0.56	O
52	Ag-0.2at%Bi-0.5at%Y-0.5at%Cu alloy	0.52	0.57	O
53	Ag-0.2at%Bi-0.5at%Y-0.5at%Au alloy	0.51	0.55	O
54	Ag-0.2at%Sb-0.5at%Nd-0.5a5%Cu alloy	0.52	0.58	O
55	Ag-0.2at%Sb-0.5at%Nd-0.5a5%Au alloy	0.53	0.60	O
56	Ag-0.2at%Sb-0.5at%Y-0.5a5Cu alloy	0.52	0.59	O
57	Ag-0.2at%Sb-0.5at%Y-0.5a5%Au alloy	0.54	0.59	O
58	Ag-0.2at%Si alloy	0.68	1.17	X
59	Ag-0.2at%Sn alloy	0.79	1.25	X

As seen from Tables 1 through 10, Ag-based alloy films (sample Nos. 2 – 4, 6 – 8, 10 – 13, 15 – 18, 20 – 23, 25 – 28, 30 – 33, 35 – 38, 40 – 43, 45 – 48, 50 – 57) which satisfy the specifications of this invention possess high thermal conductivity, high reflectivity, and high endurance. Particularly, it can be noticed that samples Nos. 10 -14 in which rare earth element of Nd was added to Ag-Bi alloy (sample No. 3), sample Nos. 15 – 19 in which Y was added to Ag-Bi alloy, sample Nos. 30 – 34 in which Cu was added to Ag-Bi alloy, and sample Nos. 35 – 39 in which Au was added exhibit improved endurance than Ag-Bi alloy (sample No. 3). Similarly, sample Nos. 20 -24 in which Nd was added to Ag-Sb alloy (sample No. 7), sample Nos. 25 – 29 in which Y was added, sample Nos. 40 – 44 in which Cu was added, sample Nos. 45 – 49 in which Au was added showed enhanced endurance than Ag-Sb alloy (sample No. 7). Moreover, sample No. 50 in which Nd and Cu were added to Ag-Bi alloy (sample No. 3), sample No. 51 in which Nd and Au were added, sample No. 52 in which Y and Cu were added, and sample No. 53 in which Y and Au were added showed better endurance than Ag-Bi alloy (sample No. 3). Similarly, sample No. 54 in which Nd and Cu were added, sample No. 55 in which Nd and Au were added, sample No, sample No. 56 in which Y and Cu were added, and sample No. 57 in which Y and Au were added enhanced their endurance when compared to binary Ag-Sb alloy (sample No. 7).

[Experiment 6: Comparison between Bi amount in the sputtering target and Bi amount in thin film]

To compare Bi content in the sputtering target and Bi content in the film which the said sputtering target was used, Ag-based alloy films listed in Table 11 were fabricated. Material which was sampled from formed Ag-based alloy film with more than 10 mg was dissolved into a solution of nitric acid aqueous solution ($HNO_3 : H_2O = 1 : 1$). The solution with dissolved sample film was further heated at 200°C on the hot plate to complete dissolution. After cooling, Bi content was analyzed by the ICP mass spectroscopy (SEIKO INSTRUMENTS SPQ-8000). Results are shown in Table 11.

For sample No.1, since Bi content in the sputtering target was little, Bi content in formed film was accordingly little. Because sample Nos. 2 – 4 satisfied the specifications set forth in this invention, it was found that formed film contained enough amount of Bi

therein. For sample No. 5, since the Bi content was too large in the sputtering target, it was found that the Bi content in the formed film was excessive.

Table 11. Comparison between Bi amount in the sputtering target and Bi amount in thin film

Experimental No.	composition	Bi [at%] in thin film
1	Ag-0.01at%Bi alloy	<0.001
2	Ag-0.05at%Bi alloy	0.005
3	Ag-1.41at%Bi alloy	0.056
4	Ag-4.50at%Bi alloy	0.398
5	Ag-7.00at%Bi alloy	1.02

[Effect of The Invention]

The As-based alloy reflective film or semi-transparent reflective film for the photo information memory medium of this invention possess high thermal conductivity, high reflectivity, and high endurance, so that memory-reproduction characteristics as well as reliability of photo information memory medium (particularly, the high-speed DVD or the next generation photo discs) can be enhanced. Furthermore, Ag-based alloy sputtering target for photo information memory medium of this invention was suitably applicable for forming the said reflective film or semi-transparent reflective film. The reflective film or semi-transparent reflective film for which the said sputtering target was used shows excellent in-film homogeneity of alloying element compositions, alloying element distribution, as well as thickness, and impurity level was very low; leading to excellent characteristics (high thermal conductivity, high reflectivity, high endurance). Hence, all these properties make it possible to produce photo information memory media with high performance and high reliability. Moreover, with such newly developed photo information memory medium systems being furnished by the reflective film or semi-transparent reflective film, the memory-reproduction characteristic and reliability can be remarkably enhanced.